

WE CLAIM:

1. An integrated process for producing LNG products in a LNG Phase production zone and GTL products that include methanol in a GTL Phase production zone from a natural gas comprising hydrocarbons and CO<sub>2</sub>, the process comprising the steps of:

pre-treating at least a first portion of the natural gas to separate at least a portion of the CO<sub>2</sub> therefrom and produce a natural gas feed having reduced CO<sub>2</sub> content and a stream rich in CO<sub>2</sub>;

converting the natural gas feed into an LNG product in the LNG Phase;

converting a second portion of the natural gas to a synthesis gas by steam methane reformation; and

reacting the stream rich in CO<sub>2</sub> with at least a portion of the synthesis gas in the GTL Phase to produce methanol.

2. The integrated process of Claim 1 further comprising feeding the stream rich in CO<sub>2</sub> with the second portion of the natural gas such that the stream rich in CO<sub>2</sub> is mixed therewith prior to formation of the synthesis gas.

3. The integrated process of Claim 1 wherein the natural gas has a methane content of at least 75 mole percent.

4. The integrated process of Claim 1 wherein after pre-treatment, the natural gas feed having reduced CO<sub>2</sub> content has a CO<sub>2</sub> content of less than 0.01 mole percent based on the total feed.

5. The integrated process of Claim 1 wherein the synthesis gas has a stoichiometric molar ratio of from about 1.5 to about 2.5.

6. The integrated process of Claim 1 wherein the synthesis gas has a stoichiometric molar ratio of from about 2.0 to about 2.1.

7. The integrated process of Claim 1 wherein the steam methane reforming is conducted by reacting steam and the natural gas over a reduced nickel-containing catalyst at a temperature in excess of 500°F and a pressure of from between 50 psig and 1000 psig.

8. The integrated process of Claim 7 wherein the temperature is from 1500°F to 1900°F.

9. The integrated process of Claim 7 wherein the pressure is from 250 psig to 600 psig.

10. The integrated process of Claim 1 wherein the second portion of the natural gas is also pre-treated to separate at least a portion of the CO<sub>2</sub> therefrom.

11. The integrated process of Claim 1 wherein all of the natural gas employed in the integrated process is initially pre-treated to remove CO<sub>2</sub> therefrom, and the second portion of the natural gas is a portion of the natural gas feed resulting from pre-treatment of the natural gas.

12. An integrated process for producing LNG products in a LNG Phase production zone and GTL products that include methanol in a GTL Phase production zone from a natural gas comprising hydrocarbons and CO<sub>2</sub>, the process comprising the steps of:

pre-treating at least a first portion of the natural gas to separate at least a portion of the CO<sub>2</sub> therefrom and produce a natural gas feed having reduced CO<sub>2</sub> content and a stream rich in CO<sub>2</sub>;

converting the natural gas feed into at least one natural gas vapor component and an LNG product in the LNG Phase;

converting the at least one natural gas vapor component, and optionally a second portion of the natural gas, to a synthesis gas by steam methane reformation; and

reacting the stream rich in CO<sub>2</sub> with at least a portion of the synthesis gas in the GTL Phase to produce methanol.

13. The integrated process of Claim 12 wherein a second portion of the natural gas is converted to synthesis gas.

14. The integrated process of Claim 13 wherein the second portion of the natural gas is pre-treated to separate at least a portion of the CO<sub>2</sub> therefrom.

15. The integrated process of Claim 13 wherein all of the natural gas employed in the integrated process is initially pre-treated to remove CO<sub>2</sub>

therefrom, and the second portion of the natural gas is a portion of the natural gas feed resulting from pre-treatment of the natural gas.

16. The integrated process of Claim 12 wherein:

conversion of the at least one natural gas vapor component and optional second portion of the natural gas to synthesis gas further comprises:

a pre-reforming step for reducing the molar concentration of ethane and higher boiling point hydrocarbon in the at least one natural gas vapor component and optional second portion of the natural gas to produce a pre-reformed natural gas vapor; and

a reforming step for converting at least a portion of the pre-reformed natural gas vapor to synthesis gas;

the reacting step further comprises:

reacting at least a portion of the synthesis gas and the stream rich in CO<sub>2</sub> to produce methanol, optionally at least one other GTL product, and a stream of unconverted synthesis gas; and

a recycling step is employed wherein at least a portion of the stream of unconverted synthesis gas is recycled to either the pre-reforming step or the reforming step,

wherein at least a portion of the at least one natural gas vapor component is directed to at least one step selected from the pre-reforming step, the reforming step, or the recycling step.

17. The integrated process of Claim 16 further comprising feeding the stream rich in CO<sub>2</sub> with the one or more of the expansion/separation cycle natural gas vapor components such that the stream rich in CO<sub>2</sub> is mixed with the vapor components prior to the pre-reforming step.

18. The integrated process of Claim 16 further comprising feeding the stream rich in CO<sub>2</sub> with the pre-reformed natural gas vapor such that the stream rich in CO<sub>2</sub> is mixed with the gas vapor prior to the reforming step.

19. The integrated process of Claim 16 wherein the recycling step comprises a compression step for recycling the stream of unconverted synthesis gas and the one or more of the natural gas vapor components is added upstream of the compression step.

20. The integrated process of Claim 16 wherein at least a portion of the optional GTL product is at least one member selected from the group consisting of products of a Fischer Tropsch reaction, dimethyl ether, and hydrogen.

21. The integrated process of Claim 12 wherein conversion of the natural gas feed in the LNG Phase comprises the steps of:

cooling the natural gas feed in at least one cooling step so as to provide a cooled natural gas stream;

processing the cooled natural gas stream in at least two expansion/separation cycles, each expansion/separation cycle comprising the substeps of:

- a. isentropically or isenthalpically expanding at least a portion of the cooled natural gas stream and producing a natural gas vapor component and a LNG component;
- b. separating at least a portion of the natural gas vapor component from the LNG component; and
- c. repeating substeps a. through b.,

wherein at least a portion of the LNG component from the previous expansion/separation cycle is directed to each successive Substep a., and

wherein the LNG product is the LNG component after the final separating step and is substantially liquid at substantially atmospheric pressure.

22. The integrated process of Claim 21 further comprising feeding the stream rich in CO<sub>2</sub> with the one or more of the expansion/separation cycle natural gas vapor components such that the stream rich in CO<sub>2</sub> is mixed with the vapor components prior to formation of the synthesis gas.

23. The integrated process of Claim 21 wherein each of the expansion/separation cycles comprise an isenthalpic expansion of the cooled natural gas streams and the LNG components across a Joule Thompson valve wherein the pressure of the cooled natural gas stream and each successive LNG component are each reduced by at least 15 psig.

24. The integrated process of Claim 21 wherein the first expansion/separation cycle comprises reducing the pressure of the cooled natural gas stream by at least 30 psig and reducing the temperature of such cooled natural gas stream by at least 10 °F.

25. The integrated process of Claim 21 wherein the expanded pressure of the natural gas vapor component and the LNG component from the first expansion/separation cycle step is not less than 75 psia.

26. The integrated process of Claim 12 wherein conversion of the natural gas feed in the LNG Phase comprises the steps of:

cooling the natural gas feed in at least one cooling step so as to provide a cooled natural gas stream;

isentropically or isenthalpically expanding at least a portion of the cooled natural gas stream in a first expansion step and producing a first natural gas vapor component and a first LNG component;

separating at least a portion of the first natural gas vapor component from the first LNG component;

isentropically or isenthalpically expanding at least a portion of the first LNG component in a second expansion step and producing a second natural gas vapor component and a second LNG component; and

separating at least a portion of the second natural gas vapor component from the second LNG component,

wherein the LNG product is the LNG component after the final separating step and is substantially liquid at substantially atmospheric pressure.

27. The integrated process of Claim 26 further comprising feeding the stream rich in CO<sub>2</sub> with the one or more of the expansion/separation cycle natural gas vapor components such that the stream rich in CO<sub>2</sub> is mixed with the vapor components prior to formation of the synthesis gas.

28. The integrated process of Claim 26 wherein the first and second expansion steps each comprise an isenthalpic expansion of the cooled natural gas stream and the first LNG component across a Joule Thompson valve wherein the pressure of the cooled natural gas stream and the first LNG component are each reduced by at least 15 psig.

29. The integrated process of Claim 26 wherein the first expansion step comprises reducing the pressure of such cooled natural gas stream by at least 30 psig and reducing the temperature of such cooled natural gas stream by at least 10 °F.

30. The integrated process of Claim 26 wherein the first natural gas component comprises a higher mole percent of nitrogen and a lower mole percent of ethane and all higher boiling point hydrocarbon than the cooled natural gas stream.

31. The integrated process of Claim 26 wherein the expanded pressure of the first expansion step is not less than 75 psia.

32. The integrated process of Claim 26 wherein at least a portion of the first natural gas vapor component becomes a fuel source for at least one



member selected from the group consisting of a LNG refrigeration compressor and the reforming step.

33. The integrated process of Claim 12 wherein conversion of the natural gas feed in the LNG Phase comprises the steps of:

cooling the natural gas feed in at least one cooling step so as to provide a cooled natural gas stream;

isentropically or isenthalpically expanding at least a portion of the cooled natural gas stream in a first autorefrigeration step and producing a first natural gas vapor component and a first LNG component;

separating at least a portion of the first natural gas vapor component from the first LNG component;

isentropically or isenthalpically expanding at least a portion of the first LNG component in a second autorefrigeration step and producing a second natural gas vapor component and a second LNG component;

separating at least a portion of the second natural gas vapor component from the second LNG component; and

compressing at least a portion of one or more of the first and second natural gas vapor components and producing a compressed natural gas feedstock having a higher temperature than either of the first and second natural gas vapor components,

wherein the LNG product is the second LNG component and is substantially liquid at substantially atmospheric pressure.

34. The integrated process of Claim 33 further comprising feeding the stream rich in CO<sub>2</sub> into the one or more of the natural gas vapor components such that the stream rich in CO<sub>2</sub> is commingled with the vapor components prior to formation of the synthesis gas.

35. The integrated process of Claim 33 wherein the expanded pressure of the first expansion step is not less than 75 psia.

36. The integrated process of Claim 33 wherein:

the temperature of the cooled natural gas stream is not more than -20 °F;

the temperature of the cooled natural gas stream is reduced by at least 3 °F in the first autorefrigeration step; and

the temperature of the second natural gas vapor component is at least 3 °F below that of the first LNG component.

37. The integrated process of Claim 33 wherein the first and second autorefrigeration steps each comprise an isenthalpic expansion of the cooled natural gas stream and the first LNG component across a Joule Thompson valve wherein the pressure of the cooled natural gas stream and the first LNG component are each reduced by at least 15 psig.

38. The integrated process of Claim 33 wherein the first autorefrigeration step comprises reducing the pressure of such cooled natural

gas stream by at least 30 psig and reducing the temperature of such cooled natural gas stream by at least 10 °F.

39. The integrated process of Claim 33 wherein:

conversion of the at least one natural gas vapor component and optional second portion of the natural gas to synthesis gas further comprises:

a pre-reforming step for reducing the molar concentration of ethane and higher boiling point hydrocarbon of the compressed natural gas feedstock and producing a pre-reformed natural gas feedstock; and

a reforming step for converting at least a portion of the pre-reformed natural gas feedstock to synthesis gas;

the reacting step further comprises:

a conversion step wherein at least a portion of the synthesis gas and the stream rich in CO<sub>2</sub> are reacted to produce methanol and a stream of unconverted synthesis gas, and at least one other reaction step selected from conversion of the synthesis gas to (i) hydrogen, (ii) dimethyl ether, or (iii) a product of a Fischer Tropsch reaction, the other reaction step converting the synthesis gas into the GTL product and a stream of unconverted synthesis gas; and

a recycling step is employed wherein at least a portion of the stream of unconverted synthesis gas is recycled to either the pre-reforming step or the reforming step,

wherein at least a portion of the compressed natural gas feedstock is directed to at least one step selected from the pre-reforming step, the reforming step, or the recycling step.

40. The integrated process of Claim 39 further comprising feeding the stream rich in CO<sub>2</sub> with the compressed natural gas feedstock such that the stream rich in CO<sub>2</sub> is mixed with the feedstock prior to the pre-reforming step.

41. The integrated process of Claim 39 further comprising feeding the stream rich in CO<sub>2</sub> with the pre-reformed natural gas feedstock such that the stream rich in CO<sub>2</sub> is mixed with the feedstock prior to the reforming step.

42. The integrated process of Claim 12 wherein conversion of the natural gas feed in the LNG Phase comprises the steps of:

cooling the natural gas feed in at least one cooling step so as to provide a cooled natural gas stream;

isentropically or isenthalpically expanding at least a portion of the cooled natural gas stream in a first autorefrigeration step and producing a first natural gas vapor component and a first LNG component;

separating at least a portion of the first natural gas vapor component from the first LNG component;

isentropically or isenthalpically expanding at least a portion of the first LNG component in a second autorefrigeration step and producing a second natural gas vapor component and a second LNG component;

separating at least a portion of the second natural gas vapor component from the second LNG component;

isentropically or isenthalpically expanding at least a portion of the second LNG component in a third autorefrigeration step and producing a third natural gas vapor component and a LNG product; and

separating at least a portion of the third natural gas vapor component from the LNG product.

43. The integrated process of Claim 42 further comprising feeding the stream rich in CO<sub>2</sub> with the one or more of the natural gas vapor components such that the stream rich in CO<sub>2</sub> is mixed with the vapor components prior to formation of the synthesis gas.

44. The integrated process of Claim 42 wherein the LNG product is substantially liquid at substantially atmospheric pressure.

45. The integrated process of Claim 42 wherein the portion of one or more of the first, second and third natural gas vapor components is compressed producing a compressed GTL feedstock having a higher temperature than any of the first, second and third natural gas vapor components exiting the first, second and third autorefrigeration steps.

46. The integrated process of Claim 42 wherein at least a portion of either or both of the first or second natural gas vapor components is converted into GTL product and at least a portion of the third natural gas vapor is compressed, refrigerated and directed to any one or more of the cooled natural

gas stream, the first LNG component, the second LNG component, or the LNG product.